We then carefully examined the disappearance of the *b* lines, *and found that they behaved exactly as they do on the sun.* Of the three lines the most refrangible was the shortest; and shorter than this were other lines, *which one of us has not yet detected in the spectrum of the chromosphere.*

This preliminary experiment, therefore, quite justified our assumption, and must be regarded as strengthening the theory on which the assumption was based—namely, that the bulk of the absorption takes place in the photosphere, and that it and the chromosphere form the true atmosphere of the sun. In fact had the experiment been made in hydrogen instead of in air, the phenomena indicated by the telescope would have been almost perfectly reproduced; for each increase in the temperature of the spark caused the magnesium vapour to extend further from the pole, and where the lines disappeared a band was observed surmounting them, which is possibly connected with one which at times is observed in the spectrum of the chromosphere itself when the magnesium lines are not visible.

III. "On the Thermodynamic Theory of Waves of Finite Longitudinal Disturbance." By W. J. Macquorn Rankine, C.E., LL.D., F.R.SS. Lond. & Edin. Received August 13, 1869.

(Abstract.)

The object of the present investigation is to determine the relations which must exist between the laws of the elasticity and heat of any substance, gaseous, liquid, or solid, and those of the wave-like propagation of a finite longitudinal disturbance in that substance—in other words, of a disturbance consisting in displacements of particles along the direction of propagation, the velocity of displacement of the particles being so great that it is not to be neglected in comparison with the velocity of propagation. In particular, the investigation aims at ascertaining:—in the first place, what conditions as to the transfer of heat from particle to particle must be fulfilled in order that a finite longitudinal disturbance may be propagated along a prismatic or cylindrical mass without loss of energy or change of type—the word type being used to denote the relation between the extent of disturbance at a given instant of a set of particles and their respective undisturbed positions; and, secondly, according to what law the type of a wave of finite longitudinal disturbance must change when the substance through which it is propagated has, under the circumstances of the disturbance, no appreciable power of transferring heat from particle to particle, being in the condition which, in the language of thermodynamics, is called *adiabatic.* The disturbed matter in these inquiries may be conceived to be contained a straight tube of uniform cross section and indefinite length.

The investigation is facilitated by the use of a quantity which the author calls the *Mass-velocity* or *Somatic Velocity*—that is to say, the mass of matter through which a disturbance is propagated in a unit of time while advancing along a prism of the sectional area unity,—also by expressing the re-

lative positions of a series of transverse planes that travel along with a wave by means of the masses of matter contained between them, instead of by their distances apart.

Let such a transverse advancing plane coincide with that part of a wave of longitudinal disturbance at which the pressure P and bulkiness S* are equal to those corresponding to the undisturbed condition; it is shown that the value of the square of the mass-velocity is

$$m^2 = -\frac{dP}{dS}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

The linear velocity of advance of the wave is obviously mS.

Let a second transverse plane advance along with the wave in such a manner that an invariable mass of matter is contained between it and the first advancing plane. The condition of *permanence of type of disturbance* is, that the distance between those planes shall be invariable. Let $\frac{dx}{dt}$ be the rate at which that distance varies, being positive when the second plane gains on the first plane; it is shown that this quantity has the following value—

$$\frac{dx}{dt} = \frac{p-P}{m} - m(S-s); \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(B)}$$

in which p and s respectively are the pressure and bulkiness at the second plane. Hence the condition of permanence of type is expressed symbolically as follows:

$$\frac{p-P}{S-s} = -\frac{dp}{ds} = -\frac{dP}{dS} = m^2 \text{ (a constant).} \quad . \quad . \quad . \quad \text{(C)}$$

This relation between pressure and bulkiness is not fulfilled by any known substance, when either in an absolutely non-conducting state (called, in the language of thermodynamics, the *adiabatic* state) or in a state of uniform temperature. In order that it may be fulfilled, transfer of heat must go on between the particles affected by the wave-motion, in a certain manner depending on the *thermodynamic function*. The value of the thermodynamic function is

$$\phi = Jc \text{ hyp} \log \tau + \chi(\tau) + \frac{dU}{d\tau}; \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(D)}$$

in which J is the dynamical equivalent of a unit of heat, c the real specific heat of the substance, τ the absolute temperature, $\chi(\tau)$ a function of the absolute temperature, which is $=0$ for all temperatures at which the substance is capable of approximating indefinitely to the perfectly gaseous state, and U the work which the elastic forces in unity of mass of the substance are capable of doing at the constant temperature τ. The thermodynamic condition to be fulfilled by a wave of permanent type is expressed by

$$\int \tau d\phi = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(E)}$$

* The word *bulkiness* is used to denote the reciprocal of the density.

In applying this equation to particular cases, ϕ and τ are to be expressed in terms of p and s.

It is shown to be probable that the only longitudinal disturbance which can be propagated with absolute permanence of type is a sudden disturbance; and that the consequence of the non-fulfilment of the condition of permanence of type is a tendency for every wave of gradual longitudinal disturbance to convert itself by degrees into a wave of sudden disturbance. But although suddenness of disturbance may be approximated to, it cannot be absolutely and permanently realized; whence it follows that the propagation of waves of longitudinal disturbance of absolutely permanent type for an indefinite distance is impossible; and this may be the cause of the absence of longitudinal vibrations from rays of light.

The laws of the advance of *adiabatic waves* are investigated; that is, waves of longitudinal disturbance in which there is no transfer of heat, and in which consequently $d\phi=0$; and it is shown, by the aid of the equation marked (B) in this abstract, that the compressed parts of those waves tend to gain upon and at last overtake the rarefied parts, just as the crests of rolling waves in shallow water gain upon and at last break into the troughs, the consequence being a gradual conversion of the adiabatic waves into waves of sudden disturbance, followed by a mutual interference of the compressed with the rarefied parts which leads to the energy of the waves being spent in molecular agitation.

It is also shown that the extreme values of the pressure and of the bulkiness are constant during the change of type; and consequently that the respective velocities with which the plane of greatest compression gains upon and the plane of greatest rarefaction falls behind the plane of undisturbed density are uniform.

The values of the linear velocity of advance, mS, found for various modes of finite disturbance, all approximate, when the disturbance becomes indefinitely small, to the well-known value of the velocity of sound, viz. $\sqrt{\left\{\frac{dP}{d.\frac{1}{S}}\right\}}$, the relation between P and S being determined by the condition $d\phi=0$.

Supplement. Received October 1, 1869.

(Abstract.)

In this supplement the author of the paper refers to the previous investigations on waves of finite longitudinal disturbance by the following authors:—

Poisson, 'Journal de l'Ecole Polytechnique,' vol. vii. cahier 14, p. 319
Stokes, Philosophical Magazine, Nov. 1848, S. 3. vol. xxxiii. p. 349.
Airy, Philosophical Magazine, June 1849, S. 3. vol. xxxiv. p. 401.
Earnshaw, Philosophical Transactions, 1860, p. 133.

He points out to what extent the results arrived at in his own paper are

identical with those of the above-mentioned previous researches; and he claims the following results as new:—The conditions as to transfer and transformation of heat which must be fulfilled in order that permanence of type may be realized, exactly or approximately, in a wave of finite longitudinal disturbance in any elastic medium; the types of wave which enable such conditions to be fulfilled with a given law of the conduction of heat; the velocity of advance of such waves; and some special results as to the rate of change of type in adiabatic waves. He also claims as new the method of investigation by the aid of *mass-velocity* and *mass-coordinates*, which he alleges to possess great advantages in point of simplicity.

IV. "Researches into the Constitution of the Opium Bases.—Part III. On the Action of Hydrochloric Acid on Codeia." By AUGUSTUS MATTHIESSEN, F.R.S., Lecturer on Chemistry in St. Bartholomew's Hospital, and C. R. A. WRIGHT, B.Sc. Received July 23, 1869.

§ 1. *On the Action of Hydrochloric Acid on Codeia.*

In Part II. (Proc. Roy. Soc. vol. xvii. p. 460) it was shown that when codeia is heated with excess of hydrochloric acid under pressure that it splits up into chloride of methyl, water, and apomorphia, thus—

$$C_{18}H_{21}NO_3+HCl=CH_3Cl+H_2O+C_{17}H_{17}NO_2.$$

At the time it appeared probable that one of the two following reactions would first take place, forming an intermediate product:—

$$\text{I.}\quad C_{18}H_{21}NO_3+HCl=CH_3Cl+C_{17}H_{19}NO_3.$$

$$\text{II.}\quad C_{18}H_{21}NO_3 \qquad = H_2O+C_{18}H_{19}NO_2.$$

On investigation, however, it has been found that neither the one nor the other takes place, at least as the chief reaction; for by heating codeia with excess of hydrochloric acid on the water-bath, a body is obtained by the following reaction—

$$C_{18}H_{21}NO_3+HCl=H_2O+C_{18}H_{20}ClNO_2;$$

and this base, when heated under pressure with hydrochloric acid, splits up into chloride of methyl and apomorphia,

$$C_{18}H_{20}ClNO_2=CH_3Cl+C_{17}H_{17}NO_2.$$

The new base may be obtained in a state of purity thus:—codeia is heated under paraffin on the water-bath with ten to fifteen times its weight of strong hydrochloric acid for twelve to fifteen hours, and the resulting brownish liquid evaporated to dryness on the water-bath; the residue is dissolved in water, and excess of bicarbonate of sodium added, whereby a voluminous white precipitate is formed, consisting chiefly of the new base mixed with a trace of apomorphia. The filtrate contains the unaltered